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PATENT APPLICATION  
PO-7978  
LeA 36,317

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICATION OF )  
MARTIN MELCHORS ET AL ) GROUP NO.: 1713  
SERIAL NUMBER: 10/784,319 )  
FILED: FEBRUARY 20, 2004 ) EXAMINER:  
TITLE: AQUEOUS COATING COMPOSITIONS ) KELECHI CHIDI EGWIM  
BASED ON PU-PAC HYBRID )  
DISPERSIONS )

**LETTER**

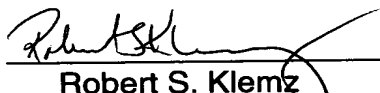
Mail Stop - Appeal Brief - Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 2231-1450

Sir:

Enclosed herewith is an Appeal Brief in the matter of the subject Appeal.

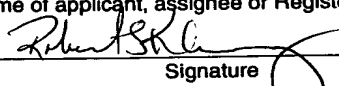
Please charge the fee for filing the Brief, \$500.00, to our Deposit Account Number 13-3848 .

Respectfully submitted

By   
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Date  
Robert S. Klemz, Reg. No. 46,305  
Name of applicant, assignee or Registered Representative  
  
Signature  
March 22, 2007  
Date



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PO-7978  
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FILED: FEBRUARY 20, 2004	)	EXAMINER:
TITLE: AQUEOUS COATING	)	KELECHI CHIDI EGWIM
COMPOSITIONS BASED ON	)	
PU-PAC HYBRID DISPERSIONS	)	

**APPEAL BRIEF**

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This Brief is in support of an appeal from the Final Office Action of the Examiner dated September 22, 2006, in which the rejection of Claims 1, 3-5 and 12 was maintained. A Notice of Appeal was filed on January 22, 2007.

**I. REAL PARTY IN INTEREST**

This application is assigned to Bayer MaterialScience AG.

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Date

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Name of applicant, assignee or Registered Representative

*Robert S. Klemz*

Signature

March 22, 2007

Date

## **II. RELATED APPEALS AND INTERFERENCES**

There are no interferences or other judicial proceedings which Appellants are aware of that may be related to, would directly affect, would be directly affected by or have a bearing on the Board's Decision in the present appeal.

## **III. STATUS OF CLAIMS**

The above-referenced application was filed with Claims 1-12.

Claims 1, 3-5 and 12 are pending but stand rejected. Claims 2 and 6-11 have been withdrawn. Claims 1, 3-5 and 12 are the subject claims of this appeal.

## **IV. STATUS OF AMENDMENTS**

No amendments were filed by Appellants after final rejection.

## **V. SUMMARY OF CLAIMED SUBJECT MATTER**

Of pending claims on Appeal, Claim 1 is the only independent claim. Claims 3-5 and 12 are dependent directly or indirectly on Claim 1. Claim 1 is directed to a method of producing aqueous, emulsifier-free and solvent-free polyurethane-polyacrylate hybrid secondary dispersions. This method of producing polyurethane-polyacrylate hybrid dispersions comprises preparing a polyurethane by reacting a polyisocyanate component with an isocyanate-reactive component. (See page 6, line 15 – page 7, line 3 of the Specification). The reaction of the two components may take place in the presence of ethylenically unsaturated monomers which are inert towards NCO groups. (See page 3, line 29- page 4, line 2 of the Specification). The isocyanate-reactive component consists of at least one of (A2) polyols or polyamines, (A3) compounds having at least one ionic or potentially ionic group, (A4) low molecular weight di- or polyols or di- or polyamines, and (A5) monoalcohols or monoamines. (See page 6, line 15 – page 7, line 3 of the Specification). The method further comprises subsequently adding unsaturated monomers to the polyurethane and subjecting the mixture to free-radical polymerization. (See page 4, lines 4 - 16 of the Specification). Finally, the polymer is optionally neutralized and dispersed in the aqueous phase. (See page 4, lines 11 - 16 of the Specification)

## **VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL**

Whether Claims 1, 3-5 and 12 are unpatentable under 35 U.S.C. §112, first paragraph as failing to comply with the written description requirement.

Whether Claims 1, 3-5 and 12 are unpatentable under 35 U.S.C. §102(b) as being anticipated by WO 2001/77200 ("Kagerer").

## **VII. ARGUMENTS**

### **CLAIMS 1, 3-5 AND 12 SATISFY THE WRITTEN DESCRIPTION REQUIREMENT UNDER 35 U.S.C. § 112, FIRST PARAGRAPH.**

Claim 1 requires that the polyurethane is prepared by reacting "the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component . . . ." The Examiner has contended that, "while being enabling for reacting the polyisocyanates with the 'at least one compound,' there is insufficient support in the originally filed disclosure for specifically reacting 'the isocyanate groups of the polyisocyanates' with the 'at least one compound.'" See Final Office Action of September 22, 2006, Paragraph 2.

A description as filed is presumed to be adequate, unless or until sufficient evidence or reasoning to the contrary has been presented by the Examiner to rebut the presumption. See *e.g.*, *In re Marzocchi*, 439 F.2d 220, 224, 169 USPQ 367, 370 (CCPA 1971); See also MPEP 2163.04. The Examiner has the burden of providing evidence of why a particular claim does not meet the written description requirement.

Original Claim 2 provides support for "preparing a polyurethane . . . by reacting . . . the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound . . ." as it required preparing the polyurethane by reacting "polyisocyanates with at least one compound containing NCO-reactive groups . . . ." Appellants submit that the

reaction of the isocyanate groups of the polyisocyanates with the isocyanate-reactive groups of the isocyanate-reactive component is inherent in such a requirement.

The reaction to prepare a polyurethane from a polyisocyanate necessarily involves reacting the isocyanate groups with isocyanate-reactive groups, as taught by virtually every organic chemistry or polymer science text that discusses polyurethanes. See e.g., Ortel, *Polyurethane Handbook*, pp. 11-17 (2<sup>nd</sup> Ed. 1994) ("The characteristic structural element of almost all of these polymers is the urethane group formed in the course of the polyaddition:  $\text{-NCO} + \text{HO-} \rightarrow \text{NH-CO-O-}$ "); Kirk-Othmer, 24 *Encyclopedia of Chemical Terminology*, at 697 (4<sup>th</sup> Ed. 1997) ("The key to the manufacture of polyurethanes is the unique reactivity of the heterocumulene groups in diisocyanates towards nucleophilic additions."). As such, it is well understood by those of ordinary skill in the art that reference to preparing a polyurethane inherently involves reacting the isocyanate groups of the polyisocyanates with isocyanate-reactive groups.

Furthermore, it would have been nonsensical for Appellants to specify that the "at least one compound" contain NCO-reactive groups if such groups were not going to react with the NCO groups of the polyisocyanates. Once again, it would be well understood by one of ordinary skill in the art, given such disclosure, and the basic nature of the polyurethane reaction, that the NCO-reactive groups are present in order to react with the NCO groups of the polyisocyanates.

Appellants have cited several instances of support for "preparing a polyurethane . . . by reacting . . . the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound . . . ." As such, Appellants respectfully request that Claims 1, 3-5 and 12 satisfy the written description requirement under 35 U.S.C. §112, first paragraph.

CLAIMS 1, 3-11 AND 13-15 ARE NOT ANTICIPATED UNDER 35 U.S.C. § 102(b) BY THE KAGERER REFERENCE (WO 2001/77200).

Kagerer discloses preparing a graft copolymer based on polyurethane that is prepared by graft copolymerizing at least one hydrophobic or hydrophilic polyurethane with at least one olefinically unsaturated monomer, in solution or in an aqueous medium. See page 2, paragraph 0023. It is an essential requirement of the teachings of Kagerer that the polyurethane contains on average at least one thiol group. See *id.* The polyurethane is prepared by reacting an isocyanate-functional prepolymer with at least one polythiol. See page 3, paragraph 0047.

In order to anticipate a claim under 35 U.S.C. § 102(b), a prior art reference must disclose every limitation of the claim. The claims of the present application require (I) preparing a polyurethane (A) . . . in non-aqueous solution, by reacting . . . the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound selected from [compounds exclusively containing isocyanate-reactive groups selected from the group consisting of –OH and –NH groups], (II) adding to the polyurethane solution (A), one or more vinylically unsaturated monomers (B) . . . and subjecting the resultant mixture to free-radical polymerization . . . , (III) optionally neutralizing . . . and (IV) dispersing the hybrid polymer in the aqueous phase . . . (*emphasis added*).

Step (I) of the process of Claim 1 clearly requires that “polyurethane (A)” is prepared by reacting . . . the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound selected from [compounds exclusively containing isocyanate-reactive groups selected from the group consisting of –OH and –NH groups]. Step (I) defines the preparation of “polyurethane (A).” In preparing “polyurethane (A),” the claims require that the isocyanate groups of polyisocyanates (A1) may only be reacted with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound selected from (A2)-(A5), all of which exclusively

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contain isocyanate-reactive groups selected from the group consisting of –OH and –NH groups. Step (I) contains no open language to allow that the polyisocyanates, at any time during the preparation of “polyurethane (A),” may be reacted with any compound containing thiol groups as the NCO-reactive groups. Thus, in the production of “polyurethane (A),” the isocyanate groups may only be reacted with –OH and –NH groups. To construe the claims in a way as to allow the isocyanate groups to reach with groups other than –OH and –NH groups would be to give no effect to the consisting of language that precedes the list of acceptable isocyanate-reactive compounds.

Step (II) of the presently claimed process requires that one or more vinylically unsaturated monomers (B) are added to “polyurethane solution (A)” (“polyurethane solution (A)” is merely “polyurethane (A)” in aqueous solution, and as required by step (I), “polyurethane (A)” does not contain thiol groups), the resultant mixture is subjected to free-radical polymerization, and the hybrid polymer is dispersed. The Examiner contends that it would be possible, presumably in a step between steps (I) and (II), to add thiol groups to the polyurethane. See Final Office Action of September 22, 2006, Paragraph 6. However, if that were the case, the resulting polyurethane would be something other than “polyurethane (A)” which is defined by its preparation in step (I). If “polyurethane (A)” was subsequently modified as suggested by the Examiner, and one were to add the monomers (B) to the hypothetical thiol-modified polyurethane, the requirement of step (II) would not be satisfied, as the monomers would be added to a polyurethane that did not meet the definition of “polyurethane (A)” as required by step (II). The claims can only be satisfied if the monomers (B) are added to “polyurethane (A)” as defined by step (I). Thus, the present claims do exclude the addition of thiol groups to the polyurethane prior to addition of the monomers.

Furthermore, step (I) further requires that “polyurethane (A)” contains no polymerizable double bonds. So, Appellants believe that the Examiner’s hypothetical step of “adding a thiol reactant to the intermediate polyurethane, in order to further grow the polyurethane prior to [step (II)]” would not result in the

polyurethane having thiol functionality, as there are no reactive double bonds present in "polyurethane (A)" to react with the thiol reactant.

The Examiner also contends that the claims are anticipated because Kagerer teaches preparing, as an intermediate, a polyurethane without thiol groups. See Final Office Action of September 22, 2006, Paragraph 6. But, the present claims require more than the preparation of a polyurethane without thiol groups. As discussed above, step (II) requires that one or more vinylically unsaturated monomers (B) are added to the "polyurethane solution (A)" (which, as defined by step (I), does not contain thiol groups), the resultant mixture is subjected to free-radical polymerization, and the hybrid polymer is dispersed. However, Kagerer does not disclose or suggest any step that meets the requirement of step (II), namely, that one or more vinylically unsaturated monomers (B) are added to "polyurethane (a)" (having no thiol groups), and the resultant mixture is subjected to free-radical polymerization.

Kagerer is very clear that the polyurethanes that are added to the olefinically unsaturated monomer must contain at least one thiol group. See e.g., page 6, paragraphs 0093 and 0094 ("The polyurethanes containing thiol groups are used to prepare the graft copolymers of the invention. For this purpose, the polyurethanes containing thiol groups are grafted in organic solution or in a dispersion with at least one monomer (a)."). The Examiner has contended that Kagerer teaches intermediate polyurethanes containing no thiol groups. See Final Office Action of September 22, 2006, Paragraph 6. However, such intermediates are not added to the olefinically unsaturated monomer. Instead, they are further reacted to impart thiol functionality to the polyurethane prior to its addition to the monomer.

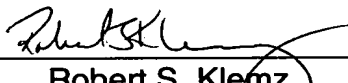
Thus, Kagerer does not teach adding a monomer to a thiol-free polyurethane, as required by the present claims. As such, Kagerer does not teach adding to the polyurethane solution (A), one or more vinylically unsaturated monomers (B) . . . and subjecting the resultant mixture to free-radical polymerization . . . , (III) optionally



neutralizing . . . and (IV) dispersing the hybrid polymer in the aqueous phase . . . as required by the present claims. As Kagerer does not disclose all of the limitations of the claimed invention, the claims cannot be anticipated by Kagerer. Appellants respectfully submit that this reference does not properly render the presently claimed invention unpatentable under 35 U.S.C. §102(b).

In view of the preceding arguments, Appellants respectfully submit that each of the Examiner's rejections is in error and respectfully request that the rejections be reversed. The allowance of Claims 1, 3-5 and 12 is respectfully requested.

Respectfully submitted,

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VIII. CLAIMS APPENDIX:

The following is a listing of the claims on Appeal.

Claim 1. A process for preparing polyurethane-polyacrylate hybrid secondary dispersions, comprising

- (I) preparing a polyurethane (A) having an average molecular weight  $M_n$  of from 1,100 to 10,000, which contains no polymerizable double bonds, in non-aqueous solution, by reacting
  - (A1) the isocyanate groups of polyisocyanates with the isocyanate-reactive groups of an isocyanate-reactive component consisting of at least one compound selected from
    - (A2) polyols and/or polyamines having an average molecular weight,  $M_n$ , of at least 400 and exclusively containing isocyanate-reactive groups selected from the group consisting of  $-OH$  and  $-NH$  groups,
    - (A3) compounds containing at least one ionic or potential ionic group and at least one other isocyanate-reactive group which are selected from mono- and dihydroxy carboxylic acids, mono- and diamino carboxylic acids, mono- and dihydroxy sulphonic acids, mono- and diamino sulphonic acids, mono- and dihydroxy phosphonic acids and mono- and diamino phosphonic acids; salts of the preceding acids; and N-methyl diethanolamine; and nonionical hydrophilic compounds containing at least one isocyanate-reactive group, which are selected from polyoxyalkylene ethers containing at least one hydroxyl or amino group,

- (A4) compounds which are different from (A3) and (A5), have a molecular weight,  $M_n$ , of less than 400, exclusively contain isocyanate-reactive groups selected from the group consisting of  $-OH$  and  $-NH$  groups, and are selected from alkane diols, alkane polyols, ether diols, ester diols, diamines and polyamines, and
- (A5) monofunctional, isocyanate-reactive compounds which are selected from monoamines and monoalcohols; and compounds which contain active hydrogen having different reactivity to isocyanate groups which are selected from compounds containing primary and secondary amino groups and compounds containing hydroxyl and amino groups, optionally in the presence of vinylically unsaturated monomers which carry no groups that are reactive towards isocyanate groups,
- (II) adding to the polyurethane solution (A), one or more vinylically unsaturated monomers (B) comprising a member selected from the group consisting of
- (B1) acid-functional monomers,
  - (B2) hydroxyl- and/or amino-functional monomers,
  - (B3) monomers other than (B1) and (B2),
- and subjecting the resultant mixture to free-radical polymerization in a homogeneous, non-aqueous phase to provide a hybrid polymer,
- (III) optionally neutralizing at least some of any potential ionic groups introduced via component (A3), and

(IV) dispersing the hybrid polymer into the aqueous phase, wherein the neutralization can take place before or after the vinyl polymerization or during the dispersing step.

Claim 2. WITHDRAWN

Claim 3. The process according to Claim 1, wherein the free-radical polymerization is conducted such that at the end the fraction of the acid-functional monomers in the monomer mixture is higher than at the beginning.

Claim 4. A polyurethane-polyacrylate hybrid secondary dispersions obtained according to the process of Claim 1.

Claim 5. The polyurethane-polyacrylate hybrid secondary dispersions according to Claim 4, wherein the hybrid polymer contains hydroxyl groups both in the polyurethane fraction (A) and in the vinylically unsaturated monomers fraction (B).

Claim 6. WITHDRAWN

Claim 7. WITHDRAWN

Claim 8. WITHDRAWN

Claim 9. WITHDRAWN

Claim 10. WITHDRAWN

Claim 11. WITHDRAWN

Claim 12. The polyurethane-polyacrylate hybrid secondary dispersions according to Claim 5, wherein vinylically unsaturated monomers (B) comprise polyacrylates.

IX. EVIDENCE APPENDIX:

1. Ortel, *Polurethane Handbook*, pp. 11-17 (2<sup>nd</sup> Ed. 1994)
2. Kirk-Othmer, 24 *Encyclopedia of Chemical Terminology*, pp. 697-700 (4<sup>th</sup> Ed. 1997).

**X. RELATED PROCEEDINGS APPENDIX:**

Appellants are unaware of any interferences or other judicial proceedings which Appellants are aware of that may be related to, would directly affect, would be directly affected by or have a bearing on the Board's decision in the present appeal. Accordingly, there is nothing to submit under this section.

# Polyurethane Handbook

Chemistry – Raw Materials – Processing  
Application – Properties

Edited by Günter Oertel

2nd Edition

With contributions from

L. Abele, Dr. G. Avar, Dr. A. Awater, Dr. G. Baatz, R. Bock, H. Boden,  
Dr. M. Dahm, Prof. Dr. D. Dieterich, Prof. Dr. W. Diller, Dr. M. Dollhausen,  
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## 2 Principles of Polyurethane Chemistry and Special Applications

Prof. Dr. D. Dieterich, Prof. Dr. E. Grigat, Dr. W. Hahn,  
Dr. H. Hespe, Dr. H. G. Schmelzer

### 2.1 Chemical Principles

Prof. Dr. E. Grigat, Prof. Dr. D. Dieterich

High molecular weight polymers based on isocyanate chemistry feature a wide variety of properties: soft to hard, plastic, elastic or thermoset, compact or foamed. They come as molded articles, film or fibers, in solutions or dispersions. Properties can be tailored to fulfill the requirements of different applications, e.g. flexible foam for upholstery, semi-rigid integral skin foam for automotive parts, rigid foam for insulation, thermoplastic elastomers, high performance rigid coatings for a diversity of substrates and requirements, flexible coatings for textile and leather, elastic fibers, and adhesives. In spite of the wide variety of applications, the chemical composition of all these products is generally quite similar. Polyurethanes are prepared by polyaddition polymerization [1] which was discovered by *Otto Bayer* in 1937. In the polyaddition process, two- or poly-functional hydroxyl- or amino-group containing compounds are reacted with di- or polyisocyanates.

#### 2.1.1 The Term "Polyurethanes"

The general term "polyurethanes" (PUR) has become known for a multitude of polymers prepared according to the diisocyanate-polyaddition principle. Polyurethanes are a wide variety of polymers with quite different compositions and correspondingly different properties. The multitude of building blocks and the possibility of designed polymerization by formation of stable intermediates (prepolymers) are features which are unsurpassed by any other polymer. The same is true concerning the adaptability in processing and composition to fulfill the widest variety of product requirements.

The characteristic structural element of almost all of these polymers is the urethane group formed in the course of the polyaddition:



Compared with other functional groups like ether-, ester-, and recently also urea-groups, the urethane groups represent often only a minor portion of the total composition (e.g. 4–6% in flexible foams). Accordingly, the properties are not significantly affected by the urethane groups. In practice, polymers containing no or very low amounts of urethane-groups are also classified as polyurethanes, as long as these products are derived from difunctional or polyfunctional isocyanates. Examples are:

Polyetherureas  
Polyureas

Polyisocyanurates  
Polycarbodiimides

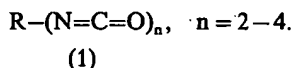
The increasing importance of di- or poly-amines as well as water used as coreactants results in the fact that most of the commercially produced "polyurethanes" contain urea groups (including isocyanurates which are cyclic ureas). Urea groups are essential structural units affecting the property profile of the resulting products. Polyurethane is the commonly used term for the final product, e.g. for foams or coatings. These products neither contain monomeric isocyanates nor biologically available isocyanate groups. In adhesives and coatings



applications the terms "polyurethane adhesives", "polyurethane hardeners" or "polyurethane coatings" are also often used for the polymer precursors. This terminology is applied as an indicator for the special properties of the final product.

### 2.1.2 Basic Reactions of the Isocyanate Groups

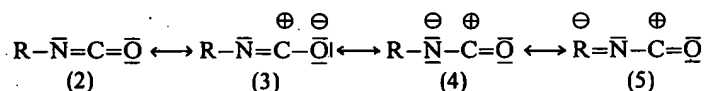
For a better understanding of polyurethane chemistry, the few basic reactions which are relevant for the synthesis of polyurethanes are presented in this section. The key substances for this chemistry are the polyisocyanates, according to the following general formula:



Polyisocyanates have been known since the middle of the last century [2].

The very high reactivity of isocyanates, especially with nucleophilic co-reactants, has always been of intriguing interest to the organic chemist. However, polyisocyanates gained technical importance only through their use in polyaddition chemistry.

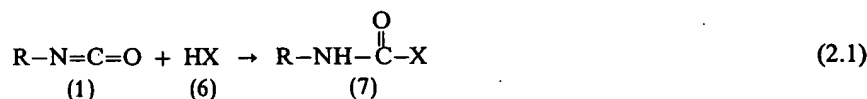
The reactivity of the  $\text{-N}=\text{C}=\text{O}$ -group is mainly determined by the pronounced positive character of the C-atom in the cumulative double bond sequence consisting of nitrogen, carbon, and oxygen. The positive charge at the C-atom becomes obvious if one looks at the resonance structure, which also indicate how substituents at the radical which bears the NCO group can influence this reactivity:



The negative charge can be delocalized into R, if R stands for an aromatic radical. This also explains the distinctly higher reactivity of aromatic isocyanates over aliphatic isocyanates. Substituents on the aromatic ring show the known influences on the positive character of the NCO group: electron withdrawing substituents in para or ortho position increase the reactivity of the NCO group, electron-donating substituents lower its reactivity. A measure of the intensity of this influence is the *Hammett* constant.

#### 2.1.2.1 Addition of Nucleophilic Reactants

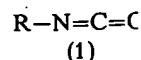
The most important reaction of isocyanates is the formation of carbamic acid derivatives (7) by the addition of components with an acidic H-atom (6) across the C-N double bond.



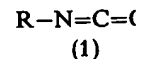
With increasing nucleophilic character of HX, this reaction occurs more easily at lower reaction temperatures. At higher temperatures, isocyanate and reactant can be regenerated. This clearly indicates that the addition reaction is a genuine equilibrium reaction [3]. The regeneration of isocyanates at elevated temperatures is used technically by capping or blocking the isocyanate with nucleophiles (e.g., phenol, oxime, lactam, CH-acidic compounds, bisulfite) which unblock readily at elevated temperatures.

The nucleophilic reaction can be strongly influenced by catalysts: acid compounds (mineral acids, acid halides, etc.) prolong the reaction [4], whereas basic compounds, especially tertiary amines, accelerate it [5]. Also metal compounds (Sn, Zn, Fe salts) have an accelerating

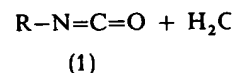
influence. The catalysts are listed in the specific section on OH group-containing compounds [3, 6]. They are added in that sequence.



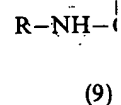
The trivial name *ureti* is used in polyurethane chemistry for more nucleophilic primary amines. In this reaction



Besides these two basic reactions, there is a third reaction which is essential for the formation of the addition product. This is the reaction of carbon dioxide, forming ureas (11) with the symmetrical urea

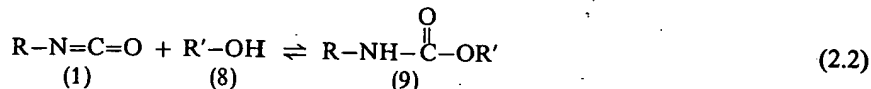


The carbon dioxide formation of the polyurethane reaction product. The reaction products are the ureas (11) still present in the starting alcohol. They are capable of reacting and are formed in the allo-



ardeners" or "polyure-  
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g general formula:



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(5)

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(2.1)

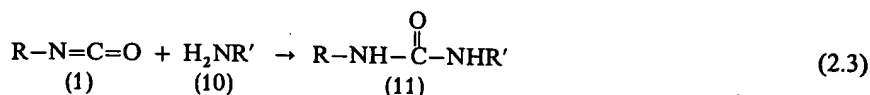
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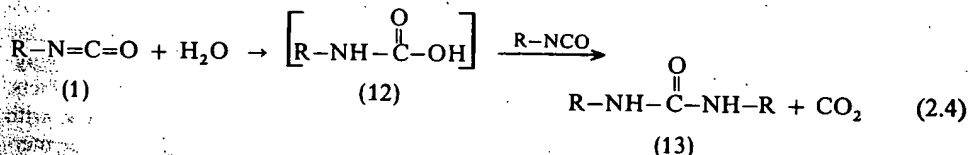
influence. The catalysis which is needed, or preferred for certain applications, will be outlined in the specific sections.

OH group-containing compounds (8) are by far the most important reactants for isocyanates [3, 6]. They are added under mild conditions to the isocyanates, forming carbamic acid esters (9). Primary alcohols, secondary alcohols, and phenols show a decreasing reactivity in that sequence.

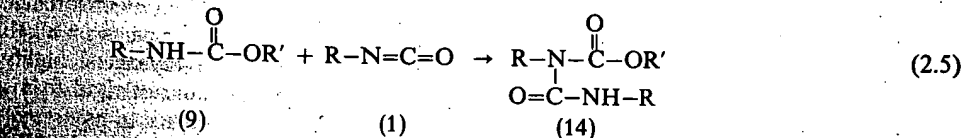
The trivial name *urethane* which is used for the compound ethyl carbamate, gave the whole polyurethane chemistry its name: polyisocyanates and polyols form polyurethanes. The much more nucleophilic primary and secondary amines react much more vigorously with isocyanates. In this reaction, ureas are formed (11) [3,7].

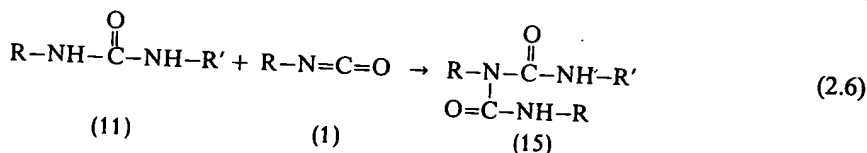


Besides these two basic reactions according to the general equation (2.1) for the addition reaction, there is a third fundamental one. This is the reaction of isocyanates with water which is essential for the formation of polyurethane foam. In this reaction, the primary addition product is the carbamic acid (12). Since carbamic acid is not stable, it splits off carbon dioxide, forming the corresponding amine. The amine immediately reacts (according to equation 2.4) with the isocyanate which is still present in the reaction mixture, forming the symmetrical urea (13) [3, 8].



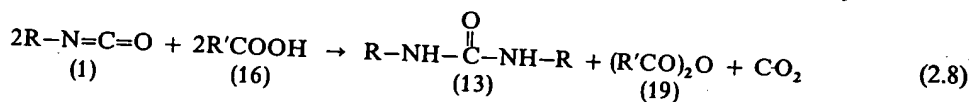
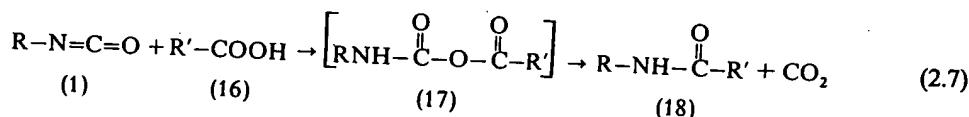
The carbon dioxide which is formed, takes over the role of a blowing agent during the formation of the polyurea which leads to the formation of the macromolecular skeleton. The reaction products according to equations (2.2) and (2.3) which are the urethanes (9) and the ureas (11) still possess acidic protons. The reactivity is significantly lower than the one of the starting alcohol, phenol, or amine, but under more rigorous reaction conditions, they are capable of reacting with additional isocyanate. The reaction products which are thus formed are the allophanates (14) from (9) and the biurets (15) from (11) [8a].





In the case of polyisocyanates, these reactions lead to branching of the polymer. At elevated temperatures, the allophanates and biurets can be split into the isocyanate and the urethane or the urea, respectively.

The reactions in equations (2.2) to (2.6) describe the essential reactions of isocyanates (1) with nucleophilic reactants. But, we also should mention the reaction of carboxylic acids (16) with isocyanates which, like the addition of water, takes place with carbon dioxide formation. Depending on the conditions, this reaction leads, via the thermally unstable mixed anhydrides (17), to the amides (18) [9, 10], or through dehydration, to carboxylic anhydrides (19) and ureas (13) [11].



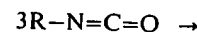
Numerous nucleophilic addition reactions have been described in the literature [12 to 14].

### 2.1.2.2 Reactions of Isocyanates with Themselves

The addition of nucleophiles to isocyanates does not cover all the important basic reactions of isocyanates. There are also reactions of isocyanates with themselves which lead to the formation of polymers and thus have gained technical importance for the formation of polyurethanes. Even the linear polymerization of monoisocyanates leads to polymer products. This reaction takes place at very low temperatures in polar solvents, such as DMF, with alkali catalysts. It leads to 1-polyamides (20) [15]. Because of their tendency to depolymerize, these polymers never gained technical importance.

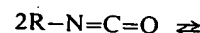


The trimerization of isocyanates to isocyanurates (21), however, is of technical importance [16]. Trimerization is catalyzed by strong bases, specifically by alkali acetates or alkali formates. The isocyanurate ring is very stable. In the case of polyisocyanates, highly branched polyisocyanurates are formed which are suited for the formation of rigid foams (polyisocyanurate foam).



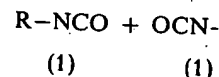
(1)

The stability of the isocyanate at higher temperatures. The reaction must be run at lower temperatures.

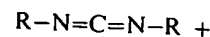


(1)

The uretdione formation is a reaction available at elevated temperatures. Different reactivity can be seen in the reaction of isocyanate groups with the formation of carbodiimides (1).



Without the presence of a catalyst, carbodiimide formation can be achieved. Methyl-3-phospholine-1-oxide can add excess isocyanates, forming a complex technically for the modification of polymers.

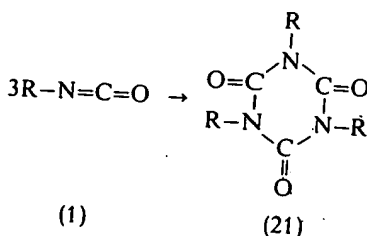


(23)

### 2.1.3 Formation of Polyisocyanates

We have explained the basic reactions of polyisocyanates and polyisocyanurates. The reaction of polyisocyanates [1] was the basic invention presented in the following equation.

(2.6)

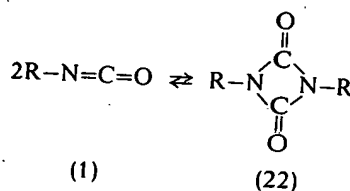


(2.10)

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anate and the urethane

ions of isocyanates (1)  
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e with carbon dioxide  
ermally unstable mixed  
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The stability of the isocyanurate ring structure permits the trimerization reaction to be run at higher temperatures. The dimerization reaction of isocyanates to uretdiones (22) [17, 18] must be run at lower temperatures because of their thermal instability.



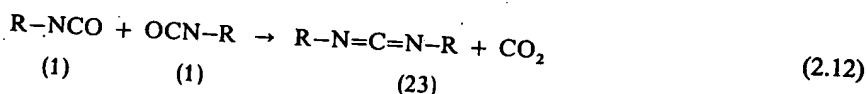
(2.11)

+ CO<sub>2</sub> (2.7)

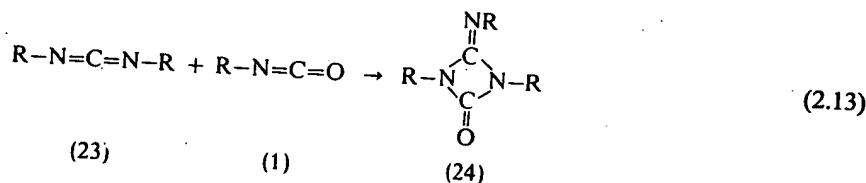
CO<sub>2</sub> (2.8)

literature [12 to 14].

The uretdione formation is a means to block isocyanates and to make the isocyanate function available at elevated temperatures. Mixtures of isocyanates which contain NCO groups of different reactivity can be separated by selective dimerization. There is another important reaction of isocyanate groups with themselves with formation of carbon dioxide: this is the formation of carbodiimides (23) [19 to 22].



Without the presence of a catalyst, this reaction takes place only at high temperatures. The carbodiimide formation can be catalyzed by special phosphorous compounds (1-ethyl-3-methyl-3-phospholine-1-oxide) so that it can be run at room temperature. Carbodiimides add excess isocyanates, forming uretone imines (24). The carbodiimide formation is used technically for the modification of polyisocyanates [23].



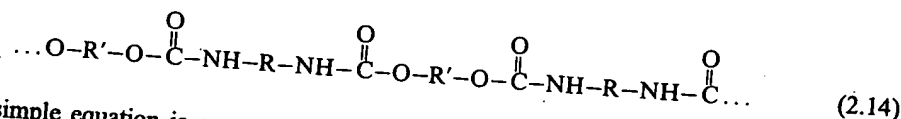
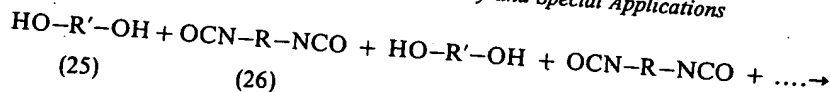
(2.9)

chnical importance  
acetates or alkali  
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on of rigid foams

### 2.1.3 Formation of Polyurethanes

We have explained the basic reactions using mono-functional reactants (Subsection 2.2.1). Polyisocyanates and poly-functional reactants undergo polyaddition leading to macromolecules. The reaction of polyisocyanates with polyols leading to the formation of polyurethanes [11] was the basic invention of *Otto Bayer*. The reaction of a diisocyanate with a diol is presented in the following equation:

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This simple equation is an expression of the principle of the polyaddition reaction which leads to an exceptional multitude of any imaginable polymer structure. As polyisocyanates, one- or multi-ring aromatic, ar-aliphatic, aliphatic, or cycloaliphatic compounds can be used. Furthermore, modified isocyanates can be used (see subsection 2.2.1). The versatility of compounds is even more extensive on the polyol side. From the two largest raw material areas, which are the polyether and the polyester polyols, there is a countless number of compounds available which differ in functionality, chain length and reactivity. Also, besides these polyether and polyester polyols, short chain diols and polyols are used for the polyaddition reactions.

Frequently, polyhydroxyl and polyamino compounds are used simultaneously resulting in polyurethane/polyureas. Finally, blends can be used not only of the hydroxyl- and amino group- containing reactants, but also on the isocyanate side. This means that the chemist has an unlimited variety of building blocks from which to select. This versatility permits the chemist to build polymers in a wide array according to specific application needs, resulting in the name "tailor-made plastics" as polyurethanes are often called. The reaction of diols with diisocyanates according to equation (2.14) leads to linear polyurethanes. If there is a tri- or polyol or a tri- or polyisocyanate present in the reaction, branching and eventually crosslinking of the polymer chains occur. The crosslink density of such a polymer depends on the amount of higher functional raw materials. This feature leads to the extension of the property spectrum of the final products.

The technical importance of polyurethane foams justifies a few additional comments with respect to their production.

The blowing of a foam requires the presence of a blowing agent. There are different methods to accomplish this:

- a) the reaction of isocyanate with water (equation 2.4) leads to carbon dioxide which can act as a blowing agent;
- b) low boiling liquids can be evaporated by the exothermically reacting mixture and thus act as blowing agents;
- c) air can be blown in or whipped into the reaction mixture forming the foam.

Today, reaction a) is preferred for the manufacture of flexible polyurethane foams. The polyurea groups which are formed by the isocyanate/water reaction contribute to the build up of the polymer skeleton (see equation 2.4).

Approach b) is the preferred blowing reaction for rigid foams. Until 1988 chlorofluoroalkanes were predominantly used, however, they have to be replaced by environmentally acceptable alternative products (see chapter 6.1.3). The combination of a) and b) allows an immediate drastic reduction of physical blowing agents. Approach c) has gained importance for the manufacturing of blown or foamed coatings. The air or the gas has to be introduced at a point when the polymer still has a sufficiently low viscosity. Balancing to achieve the optimum recipe for foam formation is very complex. Blowing reaction and polymer formation have to be coordinated by special catalysis in such a manner that both coincide. The cells have to be stabilized with special stabilizers so that they do not collapse before the cell walls have become self-supporting. Other desired properties can be obtained by certain additives, such as flame retardants, fillers and dyestuffs. Of course, these additives can influence the course of the polymer formation. The stoichiometric ratio of the isocyanate to the total

amount of active hydroxyl groups by the formation of polyurethane equivalent amounts are used. The term amount of isocyanate

## 2.2 Import

Dr. W. Hahr

### 2.2.1 Isocyanates

Isocyanates with two hydroxyl groups as one- or multi-ring aromatic and cycloaliphatic compounds, the chemistry, the properties and the availability of the aliphatic one and the aromatic one are more readily available for the polymer formation. The polymer formation is stable, light stable and has no significant differences originate from effects which can also be observed in the isocyanate more reactive than the hydroxyl group. The reactivity of the isocyanate is reacted during polyurethane formation. The phosgenation of the amines, the phosgenation, etc. [24]. These raw materials are manufactured by the catalytic reaction of methanol (MDA) via the catalytic reaction of methanol (MDA). Isophorone diisocyanate (IPDI) is used in special arrangements of nitrile compounds [28] and the all direct conversion is formally very simple and has never been used. The catalytic compound with carbonyl

amount of active hydrogen groups in the reaction mixture is of significant importance for the formation of polyurethanes and their final properties. Formulations with excess and equivalent amounts of isocyanates, as well as with sub-equivalent amounts of isocyanates, are used. The term index has been used for quite some time to express the ratio of the amount of isocyanate actually used versus the stoichiometrically calculated amount.

## 2.2 Important Building Blocks for Polyurethanes

Dr. W. Hahn

### 2.2.1 Isocyanates

Isocyanates with two or more NCO groups in the molecule are needed for the formation of polyurethanes as outlined in the preceding sections 2.1.2 and 2.1.3. Aromatic as well as aliphatic and cycloaliphatic di- and poly-isocyanates are suitable building blocks for polyurethane chemistry, the aromatic types being volumewise the more important. Reasons for this are that the aromatically linked isocyanate group is a significantly more reactive group than the aliphatic one and also that, in general terms, the aromatic isocyanates are economically more readily available. Aliphatic isocyanates are only used if their reactivity fits specifically the polymer formation or if special properties are required regarding the final products. For example, light stable coatings can only be obtained with aliphatic polyisocyanates.

There are also significant reactivity differences within the same class of isocyanates. These differences originate from their structure, from influences of substituents, and from steric effects which can also play an important role. For example, in the case of 2,4-diisocyanato toluene, the isocyanate group which is in para position to the methyl group is significantly more reactive than the isocyanate group in the ortho position (the factor is about 25). Also, the reactivity of the second NCO group of a diisocyanate can change after the first one has reacted during polyurethane formation.

Phosgenation of the corresponding amines is, as of today, still the main technical process for the *manufacture of isocyanates*. Variations of this process are the phosgenation of free amines, the phosgenation of amine hydrochlorides or carbamates, phosgenation under pressure, etc. [24]. These have been described in the technical literature. Suitable aromatic amine raw materials are manufactured preferably by the hydrogenation of the corresponding nitro compounds, for example tolylenediamine (TDA) from dinitrotoluene or diamino diphenylmethane (MDA) via the intermediate aniline derived from nitrobenzene. Aliphatic amines are manufactured by special processes. Hexamethylenediamine (HDA), for example, is produced by the catalytic reduction of adipodinitrile. Cycloaliphatic amines are in many cases available through ring hydrogenation of the corresponding aromatic amines (e.g. hydrogenated MDA). Isophorone diamine is based on acetone, hydrogen cyanide and ammonia [25]. Alternative methods to form the isocyanate group, like the *Hofmann* rearrangement [26, 29] of amides, the *Curtius* rearrangement [26, 29] of acyl azides, the rearrangement of hydroxamic acids and their derivatives (Lossen rearrangement [26, 29]), and the thermal rearrangement of nitrilo carbonates [27] are mainly of scientific interest. These reactions are only used in special cases as, for example, the Hofmann rearrangement of terephthalodiamide [28] and the alkylation of cyanates [26, 29, 30].

The direct conversion of a nitro compound into the isocyanate with carbon monoxide looks formally very simple [29, 31 to 33]. It has been known since the middle of the 1960's, but it has never been used technically because of low yields of the isocyanates and high catalyst usage. The catalytic reaction (with noble metals or selenium or sulfur as catalysts) of a nitro compound with carbon monoxide in the presence of alcohols looks technically more attrac-

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EDITOR  
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# ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME 24

THIOGLYCOLIC ACID  
TO  
VINYL POLYMERS



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and diamine  
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was introduced by the Carwin Company (later Upjohn and Dow) in 1960 under the trade name PAPI. Similar products were introduced by Bayer and ICI in Europe in the early 1960s. The superior heat resistance of rigid foams derived from PMDI prompted its exclusive use in rigid polyurethane foams. The large-scale production of PMDI made the coproduct 4,4'-methylenebis(phenyl isocyanate) (MDI) readily available, which has since been used almost exclusively in polyurethane elastomer applications. Liquid derivatives of MDI are used in RIM applications, and work has been done since the 1990s to reinforce polyurethane elastomers with glass, graphite, boron, and aramid fibers, or mica flakes, to increase stiffness and reduce thermal expansion. The higher modulus thermoset elastomers produced by reinforced reaction injection molding (RRIM) are also used in the automotive industry. In 1969 Bayer pioneered an all-plastic car having RIM-molded bumpers and fascia; in 1983 the first plastic-body commercial automobile (Pontiac Fiero) was produced in the United States.

The availability of PMDI also led to the development of polyurethane-modified isocyanurate (PUIR) foams by 1967. The PUIR foams have superior thermal stability and combustibility characteristics, which extend the use temperature of insulation foams well above 150°C. The PUIR foams are used in pipe, vessel, and solar panel insulation; glass-fiber-reinforced PUIR roofing panels having superior dimensional stability have also been developed. More recently, inexpensive polyester polyols based on residues obtained in the production of dimethyl terephthalate (DMT) have been used in the formulation of rigid polyurethane and PUIR foams.

One of the trends in polyurethanes is the gradual replacement of TDI by the less volatile PMDI or MDI in many applications. Elimination of chlorinated fluorocarbon (CFC) blowing agents and the reduction of emission of volatile organic compounds (VOCs) have been ongoing. Flexible foam producers have eliminated auxiliary blowing agents, and the rigid foam producers use water-blown formulations in combination with hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), or hydrocarbons. Adhesives and sealants are reformulated to 100% solid and water-based systems.

### Formation and Properties

**Polyurethane Formation.** The key to the manufacture of polyurethanes is the unique reactivity of the heterocumulene groups in diisocyanates toward nucleophilic additions. The polarization of the isocyanate group enhances the addition across the carbon-nitrogen double bond, which allows rapid formation of addition polymers from diisocyanates and macroglycols.



The liquid monomers are suitable for bulk polymerization processes. The reaction can be conducted in a mold (casting, reaction injection molding), continuously on a conveyor (block and panel foam production), or in an extruder

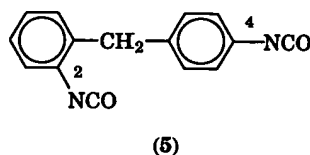
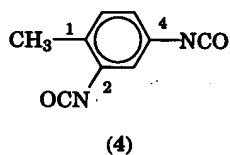
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(thermoplastic polyurethane elastomers and engineering thermoplastics). Also, spraying of the monomers onto the surface of suitable substrates provides insulation barriers or cross-linked coatings.

The polyaddition reaction is influenced by the structure and functionality of the monomers, including the location of substituents in proximity to the reactive isocyanate group (steric hindrance) and the nature of the hydroxyl group (primary or secondary). Impurities also influence the reactivity of the system; for example, acid impurities in PMDI require partial neutralization or larger amounts of the basic catalysts. The acidity in PMDI can be reduced by heat or epoxy treatment, which is best conducted in the plant. Addition of small amounts of carboxylic acid chlorides lowers the reactivity of PMDI or stabilizes isocyanate-terminated prepolymers.

The steric effects in isocyanates are best demonstrated by the formation of flexible foams from TDI. In the 2,4-isomer (4), the initial reaction occurs at the nonhindered isocyanate group in the 4-position. The unsymmetrically substituted ureas formed in the subsequent reaction with water are more soluble in the developing polymer matrix. Low density flexible foams are not readily produced from MDI or PMDI; enrichment of PMDI with the 2,4'-isomer of MDI (5) affords a steric environment similar to the one in TDI, which allows the production of low density flexible foams that have good physical properties. The use of high performance polyols based on a copolymer polyol allows production of high resiliency (HR) slabstock foam from either TDI or MDI (2).



The uncatalyzed reaction of diisocyanates with macroglycols is of no significance in the formation of polyurethanes. Tailoring of performance characteristics to improve processing and properties of polyurethane products requires the selection of efficient catalysts. In flexible foam manufacturing a combination of tin and tertiary amine catalysts are used in order to balance the gelation reaction (urethane formation) and the blowing reaction (urea formation). The tin catalysts used include dibutyltin dilaurate, dibutylbis(laurylthio)stannate, dibutyltinbis(isooctylmercapto acetate), and dibutyltinbis(isooctylmaleate). The principal tertiary amines used are listed in Table 1.

Strong bases, such as potassium acetate, potassium 2-ethylhexoate, or amine-epoxide combinations are the most useful trimerization catalysts. Also, some special tertiary amines, such as 2,4,6-tris(*N,N*-dimethylaminomethyl)-phenol (DMT-30) (6), 1,3,5-tris(3-dimethylaminopropyl)hexahydro-*s*-triazine (7), and ammonium salts (Dabco TMR) (8) are good trimerization catalysts.

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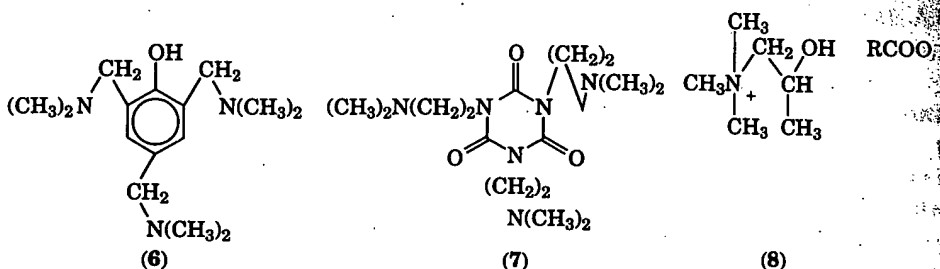
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Table 1. Tertiary Amine Catalysts for Flexible Foams

Name	CAS Registry Number	Structure	Activity	Application
Dabco			gelation catalysts	flexible foams
pentamethyldipropylene- triamine		$\begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2 \end{array}$	balanced blow and gelation catalyst	cold-cure HR foams
bis(dimethylamino ethyl ether)		$(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$	blowing catalyst	slabstock foam
pentamethyldiethylene- triamine		$\begin{array}{c} \text{CH}_3 \\   \\ (\text{CH}_3)_2\text{N}-(\text{CH}_2)_2-\text{N}-(\text{CH}_2)_2- \\ -\text{N}(\text{CH}_3)_2 \end{array}$	blowing catalyst	semiflexible foam
DBU <sup>a</sup>			heat-activated catalyst	molded foam
dimethylcyclohexylamine	[98-96-2]		balanced gelation and blowing catalyst	slabstock foam

<sup>a</sup>Phenol salt.



Hydroxy group containing tertiary amines are also used because they become incorporated into the polymer structure, which eliminates odor formation in the foam (3). Delayed-action or heat-activated catalysts are of particular interest in molded foam applications. These catalysts show low activity at room temperature but become active when the exotherm builds up. In addition to the phenol salt of DBU (4), benzoic acid salts of Dabco are also used (5).

Amine catalysts for polyurethane applications are sold by Air Products (Dabco), Abbott (Polycat), Kao Corporation (Kaolizer), Tosoh Corporation (Toyocat), and Union Carbide (Niax).

For the reaction of TDI with a polyether triol, bismuth or lead compounds can also be used. However, tin catalysts are preferred mainly because of their slight odor and the low amounts required to achieve high reaction rates. Carboxylic acid salts of calcium, cobalt, lead, manganese, zinc, and zirconium are employed as cocatalysts with tertiary amines, tin compounds, and tin-amine combinations. Carboxylic acid salts reduce cure time of rigid foam products. Organic mercury compounds are used in cast elastomers and in RIM systems to extend cream time, i.e., the time between mixing of all ingredients and the onset of creamy appearance.

The formation of cellular products also requires surfactants to facilitate the formation of small bubbles necessary for a fine-cell structure. The most effective surfactants are polyoxyalkylene-polysiloxane copolymers. The length and ethylene oxide/propylene oxide (EO/PO) ratio of the pendant polyether chains determine the emulsification and stabilizing properties. In view of the complexity of the interaction of surfactant molecules with the growing polymer chains in foam production, it is essential to design optimal surfactants for each application. Flexible polyurethane foams require surfactants that promote improved cell-wall drainage. This allows the cell walls to become more open during the foaming reaction. Also the shift away from TDI to MDI in molded high resiliency foams adds new demands on foam surfactants (6).

The physical properties of polyurethanes are derived from their molecular structure and determined by the choice of building blocks as well as the supramolecular structures caused by atomic interaction between chains. The ability to crystallize, the flexibility of the chains, and spacing of polar groups are of considerable importance, especially in linear thermoplastic materials. In rigid cross-linked systems, e.g., polyurethane foams, other factors such as density determine the final properties.

**Thermoplastic Polyurethanes.** The unique properties of polyurethanes are attributed to their long-chain structure. In segmented polyether- and polyesterurethane elastomers, hydrogen bonds form between -NH- groups

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poly(ethaned  
polycaprolact  
poly(1,6-hexa

<sup>a</sup>Mol wt = 20